

RESORCINOLIC DERIVATIVE FOR RUBBER COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to resorcinolic compounds for rubber reinforcement. More particularly, the invention relates to resorcinolic derivatives
5 that can be substituted for resorcinol during rubber manufacture; use of the present resorcinolic compounds results in enhanced cure and mechanical properties of the cured rubber compound as compared with resorcinol, while maintaining the favorable properties of uncured rubber compounds achieved when resorcinol is used.

BACKGROUND OF THE INVENTION

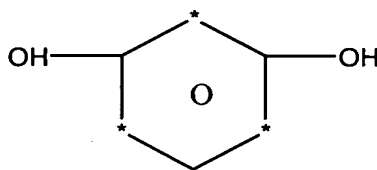
Resorcinol, resorcinolic derivatives and resorcinol-formaldehyde
resins have been used in the rubber industry as rubber compounds and adhesives. These resorcinolic compounds are unique materials in rubber compounding, since they act as thermosetting and vulcanizing plasticizers. They are very efficient
15 plasticizers for rubber during the processing operations. The use of these compounds allows easier processing, higher loading and excellent extrusions of the rubber compounds.

Resorcinol and resorcinol based derivatives and resins, which act as methylene acceptors, have thermosetting properties that, upon curing, form a resin
20 network within the rubbery polymer by reacting with various methylene donors. This results in increased hardness, abrasion resistance, aging resistance, solvent and oil resistance, and stiffness, and also gives a much improved finish to the cured rubber stock. This combination of plasticizing and reinforcing action is rare for a single material used in rubber compound formulations. In addition, resorcinolic
25 compounds may act as antioxidants when used in natural rubber.

The network formation during rubber curing is more effective with phenolic methylene acceptor compounds having meta-substitution capability than with other compounds due to their high reactivity towards methylene donors. Examples of such phenolic compounds include resorcinol, phloroglucinol and *m*-aminophenol. The use of phloroglucinol and *m*-aminophenol in rubber
30

compounding formulations is limited due to their high cost and melting points. Therefore, the most commonly employed methylene acceptor is resorcinol, due to its comparatively low cost and high reactivity. Resorcinol has three reactive sites, namely at C2, C4 and C6, indicated in formula 1 by the *:

5



TT, 0830

The high reactivity of resorcinol towards conventional methylene donors such as formaldehyde, hexamethylenetetraamine (HMTA) and hexamethoxymethylmelamine (HMMM), etc., is due to the presence of three reactive sites, meta with respect to each other, on the resorcinol molecule. The presence of two hydroxyl groups, meta with respect to each other, on the molecule further enhances the reactivity of the molecule towards methylene donors.

Though resorcinol provides enhanced physical, mechanical and adhesion properties in the cured rubber compounds, fuming associated with this material can be a problem to the tire industry. To overcome this problem, the tire industry needs compounds such as modified resorcinolic derivatives and resins that do not produce volatiles, such as those produced by resorcinol at mixing temperatures above 110°C. In addition to low volatility, the new resorcinolic compounds should have a reactivity similar to resorcinol in the rubber compound.

When the resorcinol is derivatized by attaching functional groups to either the benzene ring or hydroxyl groups, the reactivity of the resulting resorcinolic derivatives towards the methylene donor compounds is greatly reduced or altered. For example, substitutions at the 2, 4 or 6 positions of the benzene ring reduce the number of reactive sites for methylene donor interaction. Also, monoether or monoester derivatives have reduced reactivity towards methylene donor compounds as compared to resorcinol.

Resorcinol monobenzoate and derivatives of resorcinol such as resorcinol monorosinate, resorcinol diphenyl ether, resorcinol monomethyl ether, resorcinol monoacetate, phloroglucinol and derivatives used in the rubber composition are disclosed in U.S. Patent No. 4,605,696. For example, to overcome the fuming of resorcinol, monoester derivatives of resorcinol, such as resorcinol monobenzoate, were used in the rubber compound. While improved dynamic mechanical properties were observed for the cured rubber, the monoester derivatives were less reactive than resorcinol due to the presence of an ester group substituent.

U.S. Patent No. 4,892,908 discloses a keto derivative of resorcinol, namely benzoylresorcinol, which can be used as a low-fuming reinforcing material in the rubber compound. But, benzoylresorcinol has two reactive sites and a high melting point as compared to resorcinol.

U.S. Patent No. 5,049,618 discloses a vulcanizable rubber composition, which comprises rubber, a filler and N-(3-hydroxyphenyl)maleimide. N-(3-hydroxyphenyl)maleimide has three active sites for methylene donor compounds but is believed to have a higher melting point than resorcinol.

Thus, while modifications to the resorcinol molecule are expected to lower the fuming characteristics of resorcinol, they also affect the networking efficiency during curing. Therefore, it is important to develop resorcinolic compounds/derivatives that can at least maintain the reactivity of resorcinol, if not impart higher reactivities towards the methylene donor compounds. Increased reactivity of resorcinolic derivatives is expected to speed up the network formation during rubber vulcanization, which ultimately enhances the physical and mechanical properties of the cured rubber.

SUMMARY OF THE INVENTION

The present invention provides for the use of 3-hydroxydiphenylamine ("3-HDPA") in place of resorcinol to enhance the physical and mechanical properties of both uncured and cured rubber compounds. Several advantages are realized by using 3-HDPA as a methylene acceptor. For example,

3-HDPA has a lower melting point than resorcinol; this means the compound has better dispersibility or mixing with rubber compounds at a lower temperature. Because of its high molecular weight, 3-HDPA has a lower volatility than resorcinol. While 3-HDPA has the same number of reactive sites as resorcinol, it
5 has a higher reactivity, due to its being an *m*-aminophenol-type derivative.

The 3-hydroxydiphenylamines used in the present invention have been described. U.S. Patent No. 2,376,112 discloses the synthesis of 3-hydroxydiphenylamine from resorcinol and aniline using 85% phosphoric acid. U.S. Patent No. 4,265,833 outlines the preparation of various 3-
10 hydroxyphenylamines from resorcinol and aniline using a PTSA catalyst. Neither of these patents teach or suggest the use of 3-hydroxydiphenylamine as a rubber-reinforcing compound, however.

One aspect of the present invention to provide rubber compounds having enhanced physical and mechanical properties in both their cured and uncured
15 forms.

It is a further aspect of the invention to provide a method for making rubber compounds having improved physical and mechanical properties.

These and other aspects of the invention will be apparent based upon the following detailed description of the invention and appended claims.

20 DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to vulcanizable rubber compositions having improved physical and mechanical properties in both the cured and uncured forms. More specifically, the vulcanizable rubber compositions of the present invention comprise: (a) a rubber component selected from natural rubber, synthetic
25 rubber or combinations thereof; (b) a methylene donor; and (c) a methylene acceptor that is substituted or unsubstituted 3-hydroxydiphenylamine ("3-HDPA"). If substituted, the 3-HDPA contains one or more C1-6 alkyl substituents, which can be straight chain or branched, and/or can contain an additional OH group on the phenyl ring.

"Rubber" as used herein refers to both natural and synthetic rubber.

Representative synthetic rubber polymers include the butadiene polymers.

Butadiene polymers include those polymers having rubber-like properties, prepared by polymerizing butadiene alone or with one or more other polymerizable

5 ethylenically unsaturated compounds, such as styrene, methylstyrene, methyl isopropenyl ketone and acrylonitrile; the butadiene is preferably present in the mixture as at least 40% of the total polymerizable material. Other synthetic rubbers include the neoprene rubbers. Isobutylene rubber (butyl) and ethylene-propylene rubber (EPDM) may also be employed.

10 Any suitable methylene donor can be used. Methylene donors, according to the present invention, are capable of generating formaldehyde by heating during the vulcanization. Suitable examples of these methylene donors are hexamethylenetetraamine (HMTA), di- to hexamethylolmelamines or completely or partially etherified or esterified derivatives thereof, for example, hexamethoxy
15 methylmelamine (HMMM), oxazolidine derivatives, N-methyl-1,3,5-dioxazine and the like.

Typically, the methylene acceptor, namely 3-HDPA, is incorporated into the rubber component in an amount ranging from about 1 to 25 parts by weight based on 100 parts by weight of the rubber component (1 to 25 phr). Preferably,
20 the methylene acceptor is incorporated into the rubber component in an amount from about 1 to 5 phr.

Generally, the weight ratio of methylene acceptor to methylene donor is from about 1:10 to 10:1, more preferably 1:3 to 3:1. When the methylene donor is HMTA, the weight ratio is preferably at least about 2:1.

25 It will be understood by those skilled in the art that the vulcanizable rubber composition of this invention may also include one or more additives such as sulfur, carbon black, zinc oxide, silica, antioxidants, a stearate, accelerators, oils and adhesion promoters.

A preferred method of making the rubber vulcanizate is to mix the
30 rubber, carbon black, zinc oxide, lubricants and 3-HDPA in a Banbury mixer at a

temperature of about 150°C. The resulting masterbatch is then compounded on a standard 2-roll rubber mill with sulfur accelerators and formaldehyde precursor. The vulcanization composition is then shaped and then cured.

In another embodiment of this invention, a vulcanizable rubber composition is provided as described above, further comprising (d) a reinforcing material. Any reinforcing material known in the art can be used, including, but not limited to, nylon, rayon, polyester, aramid, glass, steel (brass, zinc or bronze plated) or other organic or inorganic compositions. These reinforcing materials may be in the form of filaments, fibers, cords, or fabrics.

Following formation of the rubber component, vulcanization can be carried out by methods known in the art.

The present invention is therefore further directed to a method for making a rubber composition comprising mixing: (a) a rubber component selected from natural rubber, synthetic rubber or combinations thereof; (b) a methylene donor; and (c) a methylene acceptor that is substituted or unsubstituted 3-hydroxydiphenylamine ("3-HDPA"). The ratios of methylene acceptor to rubber and methylene acceptor to methylene donor are as described above for the present rubber compounds.

3-HDPA can be prepared according to any method known in the art. Such methods are described, for example, in U.S. Patent Nos. 2,376,112 and 4,265,833, in which dihydroxybenzene and an aromatic amine are reacted. In the present method, the dihydroxybenzene is preferably resorcinol and the aromatic amine is aniline. The aniline can be substituted with one or more C₁₋₆ alkyl substituents. The resorcinol can be meta-substituted with a C₁₋₆ alkyl substituent or an additional OH moiety (i.e. phloroglucinol or 1,3,5-trihydroxybenzene). Suitable alkyl substituents are disclosed in U.S. Patent No. 4,265,833, which is hereby incorporated by reference. "Substituted 3-HDPA" as used herein refers to 3-HDPA prepared from one or both of these substituted starting materials. Preparation of the compound is further described in the examples provided below. Briefly, resorcinol,

aniline and a catalyst are mixed and heated for several hours at a temperature of between about 150-250°C.

It will be appreciated that the use of 3-HDPA in the compositions and methods described above result in a product having improved mechanical properties and enhanced cure when compared to similar compounds known in the art. The present inventors have discovered that 3-HDPA is an efficient plasticizer, offering good dispersibility with low volatility. Its high activity makes it especially suitable in network formation during the curing stage of rubber formation. Significantly, the compound offers properties to uncured rubber at least equal to if not better than resorcinol.

EXAMPLES

The following examples are intended to illustrate the invention and should not be construed as limiting the invention in any way.

EXAMPLE NO. 1

Into a 500-ml round bottomed flask equipped with a mechanical stirrer, thermometer and Dean-Stark condenser was charged 0.5 mole (55.0 grams) of resorcinol, 1.5 mole (139.7 grams) of aniline and 2.2 grams of PTSA catalyst. The reaction mixture was heated to between 185-205°C; about 11.0 grams of distillate was collected in the Dean-Stark trap in about 10.0 hours. After this, 1.0 gram of 50% wt./wt. aqueous NaOH solution was added to neutralize the catalyst. Then, vacuum was applied to distill out the excess aniline under 28" of Hg and 160-165°C temperature conditions. The final reaction product weighed 91.9 grams and showed the following composition determined by LC/GC analysis.

Composition (wt. %)

25	Aniline	5.7
	Resorcinol	6.7
	3-Hydroxydiphenylamine	89.0
	Impurity (unknown)	2.3

The melting point as determined by the capillary method was between about 65-70°C.

The above crude reaction product was recrystallized from an aqueous solution. The purified material showed a 75-79°C melting point with the following composition (wt. %):

TT, 0090⁵

Aniline	0.2
Resorcinol	0.3
Impurity (unknown)	2.1
3-Hydroxydiphenylamine	97.4

EXAMPLE NO. 2

The procedure described in Example No. 1 was repeated with 1.5
10 moles of resorcinol, 2.25 moles of aniline and 6.0 grams of PTSA catalyst. Continuous passage of nitrogen gas was done to remove the water by-product formed during the reaction. The reaction took about 21.0 hours to remove 27.1 grams of water distillate. The product weighed 280.0 grams after distilling out the excess aniline. The melting point was determined to be between 68-72°C. The
15 chemical composition determined by the LC/GC analysis showed the presence of aniline = 2.6 wt. %, resorcinol = 0.6 wt. % and unknown impurities = 4.0 wt. %.

Further purification of this crude material by an aqueous recrystallization method showed that the 3-hydroxydiphenylamine had a melting
20 point of 71-75°C and contained the following impurities (wt. %).

TT, 0091

Aniline	0.07
Resorcinol	0.04
Unknown	4.6

EXAMPLE NO. 3

25 Black natural rubber compounds were prepared in three stages to test the processing and reinforcing effect of 3-hydroxydiphenylamine as compared to resorcinol. The basic compound formulation is shown in Table 1.

87,0100

TABLE 1	
Rubber Compound Used in Testing	
Masterbatch	Parts by weight
1. Natural Rubber	100
2. Carbon Black (N-326)	55
3. Zinc Oxide	8
4. Stearic Acid	1
5. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	2
6. Pre-Vulcanization Inhibitor (N-(cyclohexylthio)phthalimide)	0.2
7. Polymerized 1,2-dihydro-2,2,4-trimethyl quinoline	1
8. Sulfur	2
9. TBBS (N-t-Butyl-benzothiazole sulfenamide)	1
10. HMTA (Hexamethylene tetraamine)	0.5
11. Methylene Acceptor (Resorcinolic Compound)	3

- In the first stage, the black masterbatch was mixed in a lab-size internal mixer to a dump temperature of 150°C and sheeted to a thickness of 8 mm. In the second stage, an appropriate amount of the black masterbatch for each
- 5 compound was mixed with the required level of either resorcinol or 3-HDPA on a two-roll mill at 120-125°C. The compounds were sheeted and cooled. The sulfur, accelerator and an appropriate amount of HMTA were added to the compound in the third stage, using the two-roll mill at 90-95°C. The compounds were aged overnight in a constant temperature room at 23°C and 50% relative humidity before
- 10 testing.

Table 2 illustrates the cure behavior and the physical and mechanical properties of the cured rubber compounds.

87,0101

TABLE 2		
CURE BEHAVIOR AND VULCANIZATE PROPERTIES		
Methylene Acceptor:	Resorcinol	3-Hydroxydiphenylamine
MDR Rheometer Cure @ 125°C (ASTM D-2084)		
ML,dN-m	2.8	2.86
MDR Rheometer Cure @ 150°C (ASTM D-2084)		
MH, dN-m	29.45	32.77
ML,dN-m	2.37	2.46

TS, Minutes	1.63	2.41
T'90, Minutes	7.66	7.47
Cure Rate	3.71	5
<u>Dynamic Properties-0.2% Strain**</u>		
G', MPa	17.16	20.08
Tan Delta	0.069	0.066
<u>Dynamic Properties-2.0% Strain**</u>		
G', MPa	10.13	12.02
Tan Delta	0.188	0.187
Hardness, Shore A (ASTM-D1415)	78	80
<u>Tensile Properties (ASTM D-412)</u>		
100% Modulus, MPa	4.84	5.32
300% Modulus, MPa	20.25	21.43
Strength, MPa	28.54	29.76
Elongation(%)	423	423
Energy to Break, N-m	26.3	27.44
Tear Strength (Die-C), KN/M	132.3	132.3
**Rheometrics Mechanical Spectrometer 800, 1.0 Hz and Room Temperature		

It is clear from the results in Table 2 that 3-hydroxydiphenylamine showed uncured rubber compound viscosity (ML from MDR Rheometer cure), T'90, tan delta (DMA) and tear strength properties similar to resorcinol. The 3-hydroxydiphenylamine of the present invention was observed to show significant improvement in properties such as MH, TS and cure rate (MDR data), G' (DMA data), Shore-A hardness and tensile properties as compared to resorcinol.

The improvement in properties observed with the 3-HDPA provides an advantage because the enhanced rubber compound properties can be easily achieved with 3-hydroxydiphenylamine without increasing the uncured rubber compound viscosity associated with resorcinol.

EXAMPLE NO. 4

To further illustrate the advantages of 3-hydroxydiphenylamine in improving the cured and uncured rubber compound properties, another masterbatch was prepared (Table 3). The rubber compound was prepared in a three-stage mixing procedure as explained in Example No. 3. In addition to resorcinol, two mono-substituted resorcinolic derivatives, namely dimethylbenzylresorcinol and 2,4-

dihydroxybenzophenone, were used in the rubber compound formulations. The cure data, as well as other physical and mechanical property data, are outlined in Table 4.

TABLE 3

Rubber Compound Formulations

Masterbatch	Parts by weight
1. Natural Rubber	100
2. Carbon Black (N-220)	50
3. Zinc Oxide	3
4. Stearic Acid	2
5. N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	1
6. Akro wax 50/50	1
7. Sulfur	2
8. TBBS (N-t-Butyl-benzothiazole sulfenamide)	1
9. HMTA (Hexamethylene tetraamine)	0.5
10. Methylene Acceptor (Resorcinolic Compound)	3

TABLE 4

CURE BEHAVIOR AND VULCANIZATE PROPERTIES

Methylene Acceptor:	Resorcinol	4-Dimethylbenzyl Resorcinol	2,4-Dihydroxy Benzophenone	3-Hydroxy-diphenylamine
MDR Rheometer Cure @ 125°C (ASTM D-2084)				
ML, dN-m	2.51	2.47	2.78	2.59
MDR Rheometer Cure @ 150°C (ASTM D-2084)				
MH, dN-m	28.17	21.74	27.48	33.11
ML, dN-m	2.15	2.03	2.31	2.15
TS, Minutes	1.51	3.47	2.35	2.39
T'90, Minutes	6.11	8.6	8.29	7.07
Cure Rate	4.66	3.07	3.48	5.53
Dynamic Properties-0.2% Strain**				
G', MPa	19.02	17.17	23.23	25.11
Tan Delta	0.083	0.09	0.076	0.073
Dynamic Properties-2.0% Strain**				
G', MPa	9.92	8.8	12.19	13.9
Tan Delta	0.237	0.246	0.229	0.223
Hardness, Shore A (ASTM-D1415)	77	74	79	82

**Rheometrics Mechanical Spectrometer 800, 1.0 Hz and Room Temperature

As can be seen from Table 4, dimethylbenzyl resorcinol and 3-hydroxydiphenylamine produced uncured rubber compound viscosity (ML from MDR cure) similar to resorcinol whereas 2,4-dihydroxybenzophenone produced higher viscosity. However, all the physical and mechanical properties of the dimethylbenzyl resorcinol based compound were lower than that of resorcinol,

2,4-dihydroxybenzophenone and 3-hydroxydiphenylamine. By comparing the cure rate, MH, G' and Shore-A hardness properties, it is clear that 3-hydroxydiphenylamine showed better rubber compound properties than 2,4-dihydroxybenzophenone and resorcinol. The MDR Rheometer cure rate data clearly shows that 3-hydroxydiphenylamine has higher reactivity than resorcinol and the other resorcinol derivatives tested in this example.

The reactivity of a methylene acceptor, such as 3-hydroxydiphenylamine, is important in the *in situ* resin formation with the methylene donor, such as HMTA, to improve the hardness, tensile and dynamic mechanical properties of the cured rubber compounds.

EXAMPLE NO. 5

Fuming of resorcinol and its derivatives at rubber compound mixing temperatures above 110°C is associated with the volatile products obtained from the unreacted resorcinol. One way to determine the volatility of a material is to run the thermogravimetric analysis. Table 5 shows the thermogravimetric analysis results of resorcinol and 3-hydroxydiphenylamine carried out in a nitrogen atmosphere.

TABLE 5					
<u>Thermogravimetric Analysis Results of Resorcinol and 3-Hydroxydiphenylamine</u>					
<u>Compound</u>	<u>% Weight Loss at *</u>				
	<u>125°C</u>	<u>150°C</u>	<u>175°C</u>	<u>200°C</u>	<u>225°C</u>
1. Resorcinol	1.7	8.5	32.6	96.4	99.1
2. 3-Hydroxydiphenylamine	0.2	0.5	1.4	4.5	13.7
*Heating Rate: 10°C/Minute in Nitrogen Atmosphere					

From the Table 5 results, it is evident that the 3-hydroxydiphenylamine produces significantly less volatiles at elevated temperatures as compared to resorcinol.

Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the

art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims.

100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000